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Growth mechanism of β-SiC nanowires in SiC reticulated porous ceramics

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Abstract

Polycarbosilane (PCS) was used as a precursor to prepare SiC reticulated porous ceramics (RPCs) with in situ growth of β-SiC nanowires at 1000–1300 °C. The nanowires in diameters of ∼50 nm exist on the surface of the strut and in the fracture surface of strut in SiC RPCs. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) indicate that the nanowire consists of a twinned β-SiC, which grows along the ⟨1 1 1⟩ direction. Field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) reveal that β-SiC nanowire grows by the vapor–liquid–solid (VLS) process at low temperature. The morphologies of the nanowire formed at different temperatures testify the process. As the heat-treated temperature increased, the growth mechanism of the nanowire changes from VLS to vapor–solid (VS).

Keywords: D. SiC; Precursor; Nanowires; Growth mechanism

1. Introduction

One-dimensional SiC nanostructures, such as nanorods and nanowires, have great potential as reinforcement material in ceramics because of their superior properties comparing to their bulk counterparts. Wong et al. [1] have reported the occurrence of SiC nanorods with very high bending strength and Young's modulus (*E*) of 53.4 GPa and of 610–660 GPa, respectively. In addition, SiC nanowires exhibit good field-emitting and unique optical properties [2,3].

Several different methods have been developed for synthesising SiC nanostructures. SiC nanowiskers have been produced by carbothermal reduction of silica [4], decomposition of organic silicon compounds [5], and reactions between silicon halides and CCl_4 [6]. Recently, carbon nanotubes have been used to prepare SiC nanorods through a reaction pathways of carbon nanotubes [7,8] employing a two-step method. Dai et al. [7] have converted carbon nanotubes into SiC nanowires in diameters of 2–20 nm by reacting with Si and I_2. Han et al. [9] have synthesised SiC nanorods via a two-step process involving the generation of SiO followed by SiC growth. Meng et al. [10] have fabricated β-SiC nanorods in diameters of ∼30 nm by carbothermal reduction of sol–gel derived silica xerogels containing carbon nano-particles. Zhou et al. [11] prepared SiC nanoraods by a hot filament chemical vapor deposition (CVD) method. Very recently, a chemical vapor infiltration (CVI) technique [12] has been used for the growing of SiC nanowires on Tyranno-SA SiC fiber fabrics. However, the aboved-mentioned methods are costly or complicated and difficult for in situ application as reinforcements in ceramic composites. Otoishi and Tange [13,14] used polycarbosilane (PCS) as the source for growing nanowires and directly formed β-SiC nanowires in porous body and carbon fibers. Recently, Zhu et al. [15] used PCS as a precursor to prepare porous SiC ceramics with in situ growth of β-SiC nanowires. However, a few articles have been discussed the growth mechanism of β-SiC nanowires using PCS as a precursor according to the morphology of them formed at different temperature.

In the present work, a simple method of in situ β-SiC nanowires growth in SiC reticulated porous ceramics (RPCs) with PCS as a precursor is described. The growth mechanism of β-SiC nanowires has been studied by investigation of the microstructures and morphologies with SEM and TEM

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analyses. The growth morphology of SiC nanowires at different heat-treating temperature was used to clarify the growth process of the nanowires.

2. Experimental procedure

The SiC RPCs were fabricated by polymeric sponge replicas method. Commercial polyurethane sponges (No. 6 Plastic Factory, Shanghai, China) were chosen in this study. α-SiC powders (98.06% purity, $D_{50} = 3.26$ μm, 0.12 wt% Fe, 0.08 wt% Ni) were used as raw material. Polycarbosilane (PCS, average molecule weight ∼1250, National University of Defense Technology, China) was used as precursor and bonding material. The gasoline was selected as solvent.

PCS was dissolved in gasoline and mixed with SiC powders by ball milling to form slurries, in which SiC powders were coated by PCS films. The sponges were immersed in the above slurry. Then the sponges with slurry were passed by a preset roller to remove excess slurry. After being dried, the coated sponge substrates were heat-treated in N_2 for 30 min at 800 °C to burn out the sponge and pyrolyzed PCS, and then fired at 1000–1300 °C for 1 h.

The morphology of the products was examined with SEM (Model JXA-8100, JEOL, Tokyo, Japan), FESEM (Model JEM-6700F, JEOL) and TEM (Model JEM-2100F, JEOL). The crystal structure was studied using selected area electron diffraction (SAED) and energy dispersive X-ray spectrum (EDS) (attached to the JEM-2100F).

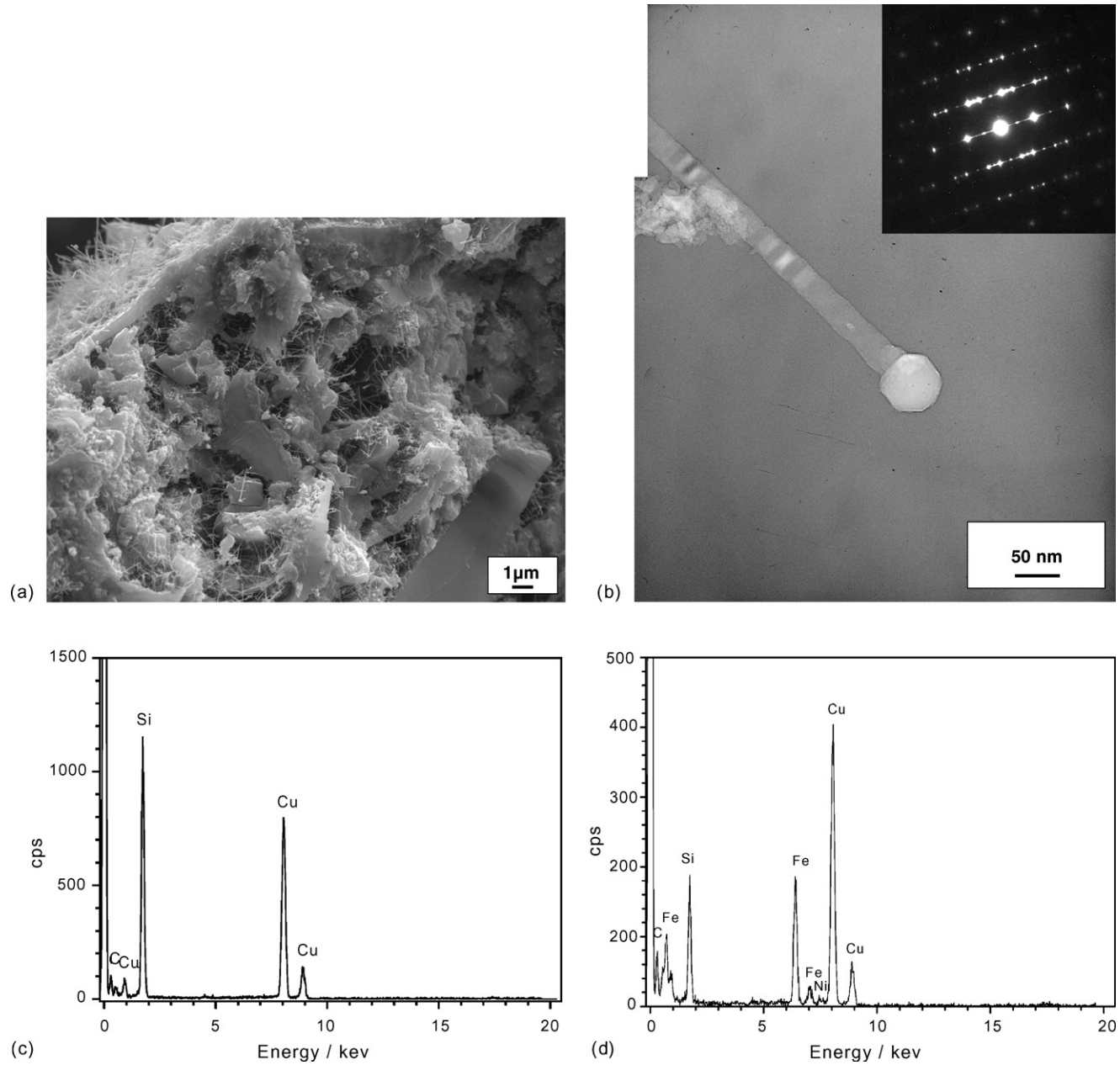

Fig. 1. (a) SEM image of the strut in SiC RPCs heat-treated at 1100 °C, (b) TEM image of a nanowire corresponding SAED, (c) EDS of the middle part of a nanowire and (d) EDS of spherical cap at the tip of a nanowire.

3. Results and discussion

Fig. 1(a) shows the fracture surface of the strut in SiC RPCs heat-treated at 1100 °C. The surface of the strut is covered with nanowires, which are randomly oriented. However, nanowires also existed in the channel of the fracture surface, which are aggregated each other. The nanowires are generally several micrometers in length and randomly oriented with straight or curved morphologies. The diameter of the nanowires is ~50 nm.

The TEM image corresponding SAED of an individual nanowires is shown in Fig. 1(b). It is shown that the nanowire is uniform over a long length with alternating bands of light and dark contrasts. The SAED pattern indicates that the nanowire consists of a β-SiC structure, companying with α-SiC structure. By calculation, the diffraction is consistent with [1 1 0] crystal band of β-SiC, which is composed of $(1\,\bar{1}\,1)$, $(1\,\bar{1}\,\bar{1})$ and (0 0 2) crystal planes. The diffraction of α-SiC is consistent with [1 0 0] crystal band, composed of (0 1 0), $(0\,0\,\bar{2})$ and $(0\,1\,\bar{1})$ crystal planes. Only the Si and C are detected by EDS analysis of the centre of the nanowire, indicating a pure Si-C chemistry in nanowires. The Cu peaks are from the copper mesh on which the crushed powders were loaded. The spherical cap containing iron and nickel is observed only on the tip of the nanowires. Iron and nickel can form low-melting point eutectic alloy at lower temperature according the Fe-Ni phase graph. A spherical cap in the tip of the nanowire and low-melting point eutectic alloy in the cap imply that the nanowire is formed by vapor–liquid–solids (VLS) mechanism. A typical VLS process starts with the dissolution of gaseous reactants into nanosized liquid droplets of a catalyst metal, followed by nucleation and growth of single-crystalline rods and then wires. The growth morphology of the nanowires at different heat-treating temperatures in Fig. 2 testified the growth process.

At 1000 °C, nanosized spherical particles and short nanowires with length lower than 300 nm are observed on the fracture surface of the strut. Each of them has a spherical cap in the tip. It can be deduced that the Fe-Ni catalyst liquid droplets were formed under 1000 °C, then the SiO and CO gas, which were caused by the process of pyrolyzation of PCS [14], dissolved into droplets to form β-SiC nanocrystal:

$$SiO + 3CO \rightarrow SiC + 2CO_2 \quad (1)$$

As the temperature increased, the concentration of β-SiC nanocrystal was supersaturated in the catalyst liquid droplets, which grew along the thermodynamically favorable direction to form nanowires at the solid–liquid interface at 1000 °C.

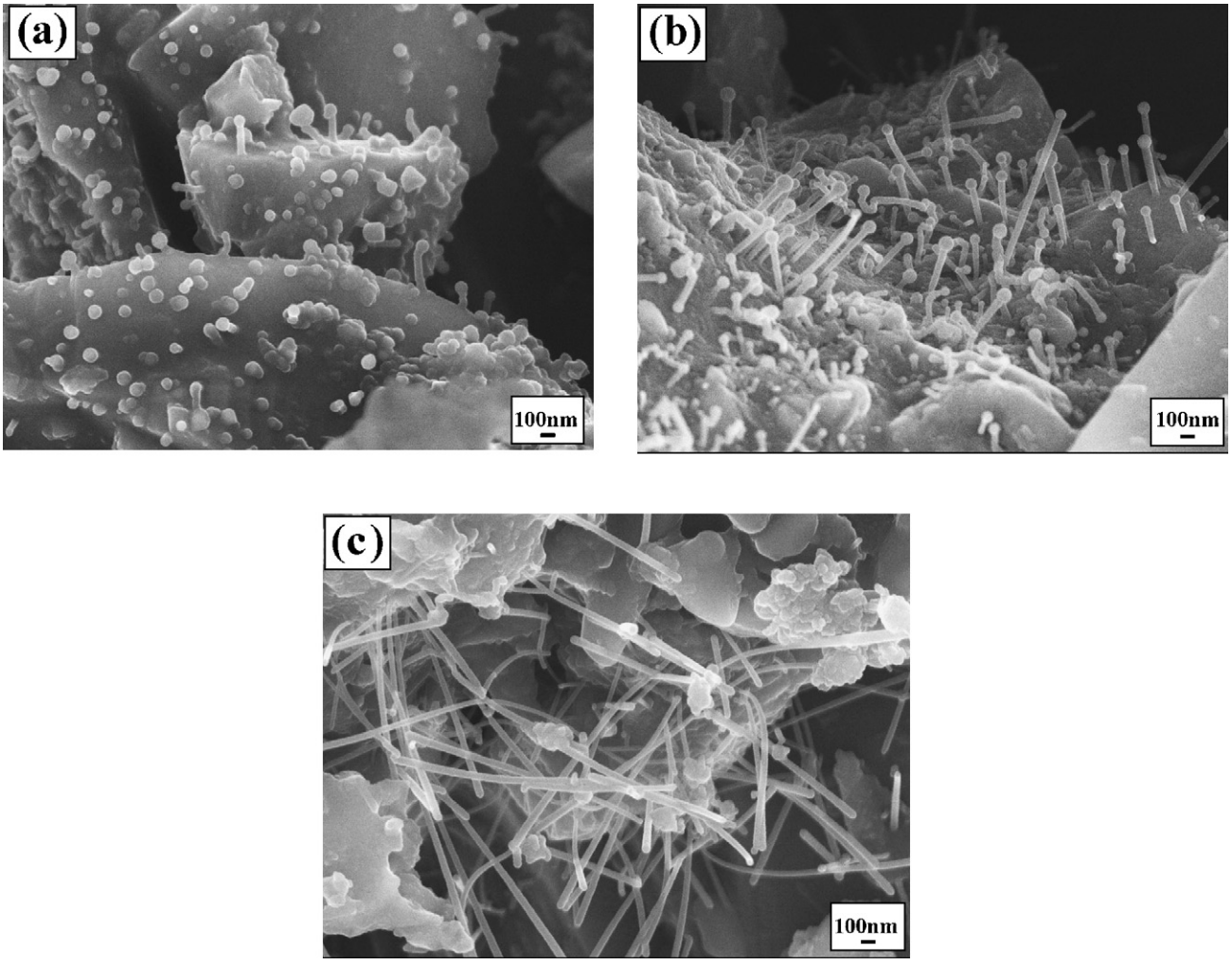

Fig. 2. FESEM images of β-SiC nanostructures formed at (a) 1000 °C, (b) 1100 °C and (c) 1300 °C.

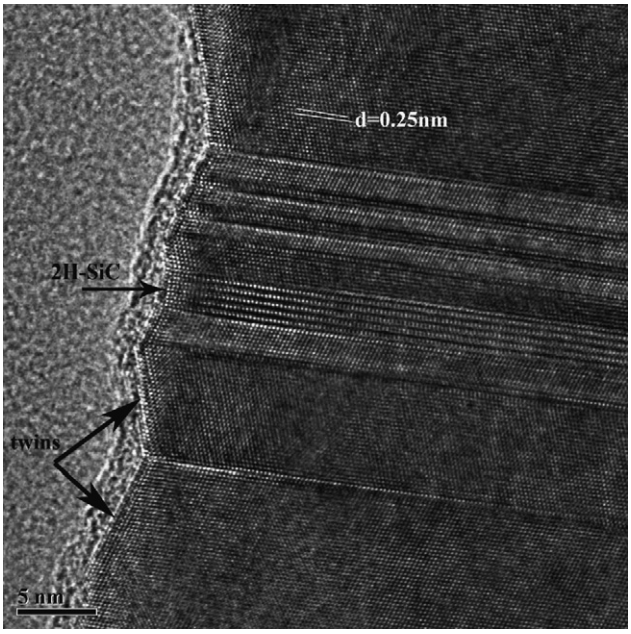

Fig. 3. HRTEM image of a nanowire.

As the heat-treating temperatures gradually increase, the nanowires grow and become longer. At 1100 °C, a large amount of nanowires with straight and curved shape have been formed, and all of them also have spherical caps in the tips. According to Yang's work [16], the curved growth results from a fluctuation of the kinetic growth condition, which is caused by the fluctuation of β-SiC nanocrystals supersaturation in the crystal droplet. The supersaturation of β-SiC nanocrystals make the nanowire grow along the directions other than ⟨1 1 1⟩ direction. Under the condition, the fluctuation of supersaturation will disturb the balance between growth along different directions, which results in the curved shapes.

From Fig. 2(c), it can be seen that spherical caps are not observed on the tip of the nanowires formed at 1300 °C. At the same time, no iron and nickel are detected on the tips of the nanowires. The results suggest that the spherical caps have been evaporated from the tips of the nanowires. Therefore, it can be assumed that the growth process of nanowires changes from VLS to VS as the heat-treating temperature increased to 1300 °C.

Fig. 3 shows the HRTEM image of the SiC nanowires formed at 1100 °C. The image shows that the nanowire mainly consists of a single-crystal β-SiC structure. It possesses high-density stacking faults and twins in the crystal plane normal to the axis of the nanowire. A fluctuation of kinetic growth condition might cause a change in the stacking sequences, which results in stacking faults in the nanowire. The stacking faults, such as microtwins, have a lower energy than that of the β-SiC [16], and therefore, are helpful in maintaining lower growth energy of the nanowires. The distance between these planes is 0.25 nm, which is the same as the distance between (1 1 1) planes in a β-SiC crystal. Therefore, the nanowires grows along the ⟨1 1 1⟩ direction. Because the (1 1 1) planes have the lowest surface energy among the SiC plane, the system energy is reduced significantly when the (1 1 1) planes are parallel to the growth direction [16].

4. Conclusions

In situ nanowires growth is observed in SiC RPCs with PCS as precursor at 1000–1300 °C in the flow of N_2 gas. TEM and SAED verify that the nanowires are mainly the crystalline β-SiC structure with dense stacking faults. When the heat-treating temperature is lower than 1100 °C, a spherical cap of the nanowire and low-melting point eutectic alloy in the cap indicates that β-SiC nanowires grow by a VLS mechanism. At 1300 °C, the nanowires grow by a VS process due to the evaporation of the alloy. At higher temperature, the nanowires with curved shapes are formed, which resulted from a fluctuation of the kinetic growth condition.

Acknowledgements

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